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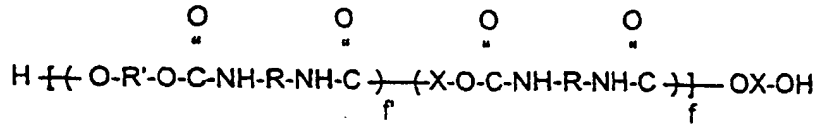
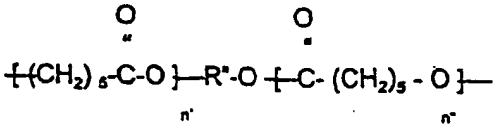
(54) POLYURETHANE CRYSTALLINE THERMOPLASTIC AND METHOD FOR THE PRODUCTION THEREOF

(57) The compound has the general formula I



(I)

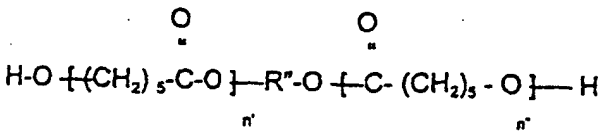
(1 < f < 58; 0 < f' < 58; R and R' are alkyl or aryl) and X has the formula II



(II)

(42 < (n' + n") < 220). The method comprises reacting a polyetherpolycaprolactone block copolymer having a molecular weight ranging from 1,000 to 6,000 and having formula IIa

EP 0 953 586 A1

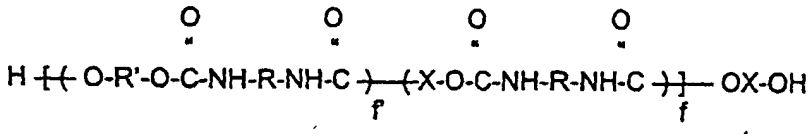


(IIa)

with a chain extender of formula HO-R'-OH and with a diisocyanate of formula OCN-R-NCO.

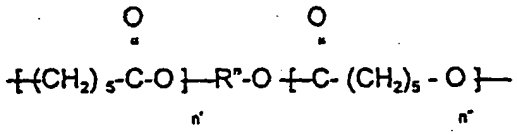
Description

[0001] The invention relates to a cystalline polyurethane thermoplastic material having the general formula I



(I)

where f is an integer ranging from 1to 58; f' is an integer ranging from 0 to 58; R and R' are the same or different and stand for alkyl or aryl groups and X is a polycaprolactone block polymer, having a molecular weight ranging from 500 to 25,000 and having formula II



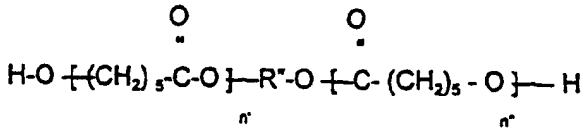
(II)

where R" is an alkyl or aryl group, and n' and n" are integers the sum of which ranges from 42 to 220.

[0002] This polyurethane is particularly useful in thermobonding and hot melt applications in the industrial markets, above all for footwear, wood and automotion.

[0003] The polyurethane thermoplastic materials of the present invention have the advantage over all the known polyurethane thermoplastic materials of being very crystalline, with good physico-chemical and mechanical properties, and at the same time very thermoplastic, with softening points of 60-70°C and very soluble in all the regularly used solvents. They are also very easily presentable in microbead form or convertible into powders.

[0004] The invention also relates to a method of preparing the said compound. This method is characterised in that it comprises reacting a polycaprolactone polymer of relatively high molecular weight



(IIa)

with a diisocyanate of formula OCN-R-NCO and optionally with a chain extender of formula HO-R'-OH, where R and R' have the same meaning as indicated hereinbefore. Said extender is preferably 1,4-butanediol and said diisocyanate is diphenylmethane 4,4'-diisocyanate, toluene 2,4- and 2,6-diisocyanate, dicyclo hexylmethane 4,4'-diisocyanate or 3-isocyanomethyl-3,5,5-trimethylcyclohexyl isocyanate.

[0005] The reaction is also preferably conducted by mixing equimolecular amounts of diisocyanate with the formula II polycaprolactone polymer.

[0006] It is contemplated that mixing be continuous with a flow rate ranging from 200 to 1200 kg/h of total component weight, in an extruder, at a temperature ranging from 150° to 350°C and with a mean dwell time ranging from 45 seconds to 2.5 minutes.

[0007] The reaction is preferably conducted in the presence of metal complex based catalysts proper to urethane reactions, particularly tin and/or bismuth derivatives.

EXAMPLE 1

Preparation of a crystalline polyurethane thermoplastic material

[0008] 87.0 kg of 2,4; 2,6 toluene diisocyanate and 5,000 kg of the polycaprolactone polymer were used. These products were mixed in a continuous process at a rate of 600 kg/h in a double screw extruder of a form proper to a reactor, at a temperature held to between 200° and 300°C and with a mean dwell time ranging from 1.5 to 2.0 minutes.

[0009] On exiting from the extruder, the product was cut, cooled and formed into beads, was dried and packaged under standard temperature and humidity conditions. An amount of 100 ppm of metal complex catalysts was used in the process.

EXAMPLE 2

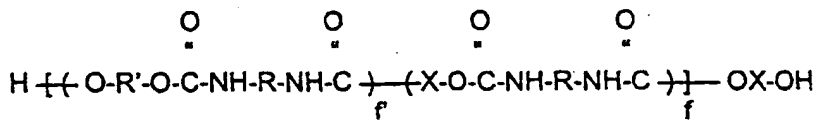
Preparation of a crystalline polyurethane thermoplastic material

[0010] 250 kg of 4,4'-diphenyl-methane diisocyanate and 10,000 kg of the polycaprolactone polymer were used. These products were mixed in a continuous process at a rate of 600 kg/h in a double screw extruder of a form proper to a reactor, at a temperature held to between 200° and 300°C and with a mean dwell time ranging from 1.5 to 2.0 minutes.

[0011] On exiting from he extruder, the product was cut, cooled and formed into beads, was dried and packaged under standard temperature and humidity conditions. an amount of 100 ppm of metal complex catalysts was used in the process.

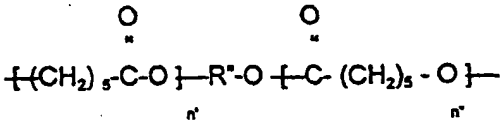
Claims

1. A crystalline polyurethane thermoplastic material having the general formula I



(I)

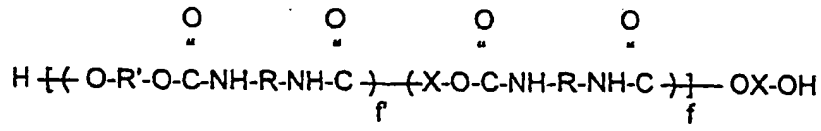
where f is an integer ranging from 1 to 58; f' is an integer ranging from 0 to 58; R and R' are the same or different and stand for alkyl or aryl groups and X has the formula II



(II)

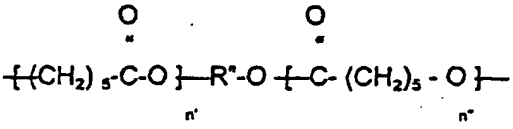
where R" is an alkyl or aryl group, and n' and n" are integers the sum of which ranges from 42 to 220.

2. A method for the preparation of a crystalline polyurethane thermoplastic material of general formula I,



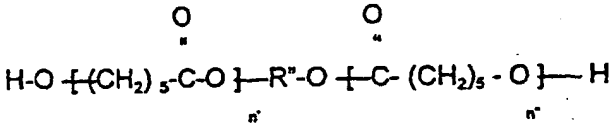
(I)

where f is an integer ranging from 1 to 58; f' is an integer ranging from 0 to 58; R and R' are the same or different and stand for alkyl or aryl groups and X has formula II



(II)

where R" is an alkyl or aryl group, and n' and n" are integers the sum of which ranges from 42 to 220, characterised in that it comprises reacting a polycaprolactone polymer of formula IIa



(IIa)

where R", n' and n" have the meaning given hereinbefore, with a diisocyanate of formula OCN-R-NCO where R and R' have the meaning given hereinbefore.

3. The method according to claim 2, characterised in that a chain extender of formula HO-R'-OH is used in said reaction between the polycaprolactone polymer of formula IIa and said diisocyanate.

4. The method according to claim 3, characterised in that said extender is 1,4-butanediol.

5. The method according to at least one of claims 2 to 4, characterised in that said diisocyanate is diphenylmethane 4,4'-diisocyanate, toluene 2,4-and 2,6-diisocyanate, dicyclo hexylmethane 4,4'-diisocyanate or 3-isocyanomethyl-3,5,5-trimethylcyclohexyl isocyanate.

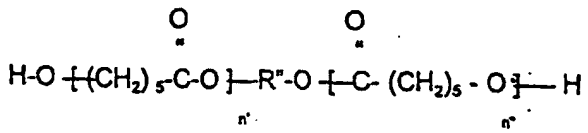
6. The method according to one of claims 2 to 5, characterised in that said reaction is conducted by mixing equimolecular amounts of diisocyanate with said chain extender and said polycaprolactone polymer of formula II, said last two compounds being present at a molar rate ranging from 0/1 to 1/1 respectively.

7. The method according to claim 6, characterised in that the mixing is continuous with a flow rate ranging from 200 to 1200 kg/h of total component weight, and is performed in an extruder, at a temperature ranging from 150° to 350°C and with a mean dwell time ranging from 45 seconds to 2.5 minutes.

8. The method according to one of claims 2 to 7, characterised in that said reaction is conducted in the presence of metal complex based catalysts proper to urethane reactions.

9. The method according to claim 8, characterised in that said metals are tin and/or bismuth.

10. The method according to one of claims 2 to 9, characterised in that said polycaprolactone polymer of formula IIa



(IIa)

where R", n' and n" have the meaning given hereinbefore, has a molecular weight ranging from 5,000 to 25,000.

INTERNATIONAL SEARCH REPORT

International application No.
PCT / ES 98/00313

A. CLASSIFICATION OF SUBJECT MATTER [6]:
IPC6: C08G 18/42, 63/02, 63/08, 63/78, 63/664
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC6: C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CIBEPAT, EPODOC, WPIL, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4098747 A (BAILEY et al.) 04.07. 1978 4 July 1978 Column3, line34-59; column 4, lines 15-19	1-10
A	EP 0492824 A (Minnesota Mining and Manufacturing Company) 01.07.1992 1 July 1992 page 5, lines 14-42; pages 6, lines 34-36, claims 1-11	1-10
A	DE 19519391 A (HENKEL KGAA) 28.11.1996 28 November 1996 Claim 4	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 February 1999 (18.02.1999)	24 February 1999 (24.02.99)
Name and mailing address of the ISA/ S.P.T.O.	Authorized officer Sonia Gonzalez Penalba
Facsimile No.	Telephone No.+ 34 91 349 54 75

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/ ES 98/00313

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		WO 9637566 A	28.11.1996

Form PCT/ISA/210 (patent family annex) (July 1992)